

THE CONSTITUTION  
OF  
CHAULMOOGRIC ACID

PART I.

BY

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AND

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THE WELLCOME CHEMICAL RESEARCH LABORATORIES

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LXXXVI.—*The Constitution of Chaulmoogric Acid.*  
*Part I.*

By FREDERICK BELDING POWER and FRANK HOWORTH GORNALL.

IN the preceding paper on the constituents of chaulmoogra seeds, from *Taraktogenos Kurzii* (King), the isolation of a new, unsaturated, fatty acid, melting at  $68^{\circ}$ , was described. This substance, designated as *chaulmoogric acid*, was shown to have the formula  $C_{18}H_{32}O_2$ , and



would thus at first sight appear to belong to the series  $C_nH_{2n-4}O_2$ , which includes its isomerides linolic and tariric acids, both of which also occur in fatty oils. These two acids, however, form tetrabromides, and, under certain conditions, combine respectively with four atomic proportions of iodine, whereas chaulmoogric acid interacts with only two atomic proportions of these elements. It therefore became evident that chaulmoogric acid possesses only one ethylenic linking, and must necessarily contain in its structure a closed ring, a conclusion which has been amply borne out by further investigation. It is the possession of the latter feature which specially differentiates chaulmoogric acid from any of the known naturally occurring fatty acids.

With the object of eventually elucidating the constitution of chaulmoogric acid, a number of its derivatives have been prepared and studied, and some of the results thus far obtained are given in this communication.

When chaulmoogric acid is treated with methyl alcohol and hydrogen chloride, *methyl chaulmoograte*,  $C_{17}H_{31} \cdot CO_2Me$ , is produced, *ethyl chaulmoograte*,  $C_{17}H_{31} \cdot CO_2Et$ , being obtained in a similar manner. *Chaulmoogramide*,  $C_{17}H_{31} \cdot CO \cdot NH_2$ , was prepared according to Aschan's method (*Ber.*, 1898, 31, 2344).

When chaulmoogric acid is treated with hydrogen bromide in glacial acetic acid, the optically inactive *bromodihydrochaulmoogric acid*,  $C_{17}H_{32}Br \cdot CO_2H$  (m. p. 36—38°), is produced.

When ethyl chaulmoograte, in chloroform solution, is treated in the cold with an excess of bromine, it readily combines with two atomic proportions of the latter, forming *ethyl dibromodihydrochaulmoograte*,  $C_{17}H_{31}Br_2 \cdot CO_2Et$ , which is a yellow oil.

When chaulmoogric acid was treated with sodium and amyl alcohol, its ethylenic linking was not resolved, but *chaulmoogryl alcohol*,  $C_{18}H_{33} \cdot OH$ , and *chaulmoogryl chaulmoograte*,  $C_{17}H_{31} \cdot CO_2 \cdot C_{18}H_{33}$ , were obtained. The former is evidently produced by the reduction of the esters of chaulmoogric acid, which would be formed in small amount by the interaction of the acid and the amyl alcohol prior to the introduction of the sodium (compare Bouveault and Blanc, *Compt. rend.*, 1903, 137, 328). The formation of chaulmoogryl chaulmoograte took place during the subsequent fractional distillation of the mixture of chaulmoogryl alcohol and unchanged chaulmoogric acid.

When, however, bromodihydrochaulmoogric acid is treated with zinc dust and alcohol, or chaulmoogric acid with hydriodic acid and phosphorus, the saturated compound, *dihydrochaulmoogric acid*,  $C_{17}H_{33} \cdot CO_2H$ , is formed; the *methyl ester*,  $C_{17}H_{33} \cdot CO_2Me$ , of the latter acid was also prepared. The last-mentioned method of reduc-

tion also yielded a hydrocarbon, *chaulmoogrene*, which, on analysis, gave figures agreeing with the formula  $C_{18}H_{34}$ .

When chaulmoogric acid was oxidised with cold permanganate in amount equivalent to 1 atomic proportion of oxygen, *dihydroxy-dihydrochaulmoogric acid*,  $C_{17}H_{31}(OH)_2 \cdot CO_2H$ , was isolated. When, however, an amount of permanganate equivalent to 4—5 atomic proportions of oxygen was employed, a mixture of several acids was obtained, from which were isolated formic acid and two dibasic acids having the formulæ  $C_{15}H_{28}(CO_2H)_2$  (*ethyl ester*,  $C_{15}H_{28}(CO_2Et)_2$ ) and  $C_{15}H_{28}O(CO_2H)_2$ . The *ethyl ester* of the latter acid,  $C_{15}H_{28}O(CO_2Et)_2$ , was also prepared.

Dr. W. H. Perkin, sen., very kindly determined for us the magnetic rotation and refractive power of ethyl chaulmoograte. The molecular rotatory power of this compound was found to approximate very closely to the calculated value for an unsaturated substance having the formula  $C_{20}H_{36}O_2$ , possessing a closed ring and one ethylenic linking, the latter being contained in an allyl group.

Dr. Perkin's suggestion that chaulmoogric acid might contain an allyl group was made prior to the isolation of formic acid and the two acids having the formulæ  $C_{17}H_{30}O_4$  and  $C_{17}H_{30}O_5$ , and these results have therefore confirmed the correctness of this assumption.

#### EXPERIMENTAL.

##### *Methyl Chaulmoograte*, $C_{17}H_{31} \cdot CO_2Me$ .

Fifteen grams of chaulmoogric acid were dissolved in 30 grams of methyl alcohol and a current of hydrogen chloride passed into the warm solution during two hours. The ester soon separated as an oily layer, which, on cooling, became solid; water was then added and the whole extracted with ether. The ethereal solution was washed successively with water, then several times with 10 per cent. aqueous sodium carbonate, and finally with water, dried, the ether removed, and the residual oil distilled under diminished pressure. It practically all passed over at  $227^\circ$  corr./20 mm. as a colourless oil, which, on cooling, formed a solid mass of needles, melting at  $22^\circ$ .

0.1185 gave 0.3368  $CO_2$  and 0.1265  $H_2O$ .  $C = 77.5$ ;  $H = 11.8$ .

0.1209 „ 0.3422  $CO_2$  „ 0.1290  $H_2O$ .  $C = 77.2$ ;  $H = 11.8$ .

$C_{19}H_{34}O_2$  requires  $C = 77.6$ ;  $H = 11.6$  per cent.

$d_{25^\circ/25^\circ} = 0.9119$ ;  $\alpha_D + 46^\circ 4'$  in a 1 dcm. tube, whence  $[\alpha]_D + 50.5^\circ$ . Five grams in 100 c.c. of chloroform gave  $\alpha_D + 1^\circ 14'$  in a 50 mm. tube, whence  $[\alpha]_D^{15^\circ} + 50^\circ$ .



*Ethyl Chaulmoograte*,  $C_{17}H_{31} \cdot CO_2Et$ .

Ethyl chaulmoograte was prepared in the same manner as the methyl ester ; it boiled at  $230^\circ$  corr./20 mm., and is a colourless oil.

0.1356 gave 0.3866  $CO_2$  and 0.1438  $H_2O$ .  $C = 77.8$  ;  $H = 11.8$ .

0.1090 „ 0.3112  $CO_2$  „ 0.1168  $H_2O$ .  $C = 77.9$  ;  $H = 11.9$ .

$C_{20}H_{36}O_2$  requires  $C = 77.9$  ;  $H = 11.7$  per cent.

$d_{15^\circ/16^\circ} = 0.9079$  ;  $\alpha_D + 46^\circ$  in a 1 dcm. tube, whence  $[\alpha]_D^{20^\circ} + 50.7^\circ$ .

A specimen of this ester was sent to Dr. W. H. Perkin, sen., who very kindly determined its density, magnetic rotation, and refractive power, with the following results :

*Density determinations*:  $d_{10^\circ/10^\circ} 0.91064$  ;  $d_{15^\circ/15^\circ} 0.90741$  ;  $d_{20^\circ/20^\circ} 0.90456$ .

*Magnetic Rotation.*

	<i>l</i> .	<i>t</i> .	Sp. rotation.	Mol. rotation.	Optical rotation.
(1)	175 mm.	$13.9^\circ$	1.1189	21.065	$[\alpha]_D + 50.69^\circ$
(2)	104 mm.	14.3	1.1115	20.976	$[\alpha]_D + 50.73$

Average molecular rotation, 21.020.

The calculated values on the basis of ethyl stearate,  $C_{20}H_{40}O_2$ , mol. rot. 20.797, (1) with two unsaturated linkings ( $-H_2 \times 2 = +1.112 \times 2$ ); (2) with ring formation ( $-0.6$ ) and a single unsaturated linking ( $-H_2 = +1.112$ ); (3) with ring formation ( $-0.6$ ) and a single allyl group ( $-H_2 = +0.913$ ), are as follows :

		Mol. rotation.
	Ethyl Stearate	20.797
(1)	Two unsaturated linkings ( $-H_2 \times 2 = +1.112 \times 2$ )	2.224
		<hr/> 23.021
	Ethyl stearate	20.797
(2)	Ring formation ( $-0.6$ )	0.600
		<hr/> 20.197
	One unsaturated linking ( $-H_2 = +1.112$ )	1.112
		<hr/> 21.309
	Ethyl stearate	20.797
(3)	Ring formation ( $-0.6$ )	0.600
		<hr/> 20.197
	One allyl group ( $-H_2 = +0.913$ )	0.913
		<hr/> 21.110

The value found, namely, 21.020, is seen to approximate very closely to the third calculated value, 21.110, which is that for an ester having the formula  $C_{20}H_{36}O_2$ , containing a closed ring and one unsaturated linking of an allylic nature.

*Refractive Power.*

$$d_{15.4^\circ/4^\circ} 0.90637.$$

	$\mu. 15.4^\circ.$	$\frac{\mu-1}{d}.$	$\frac{\mu-1}{d}^p.$
H $\alpha$ .....	1.46000	0.50752	156.315
H $\beta$ .....	1.46851	0.51691	159.208
H $\gamma$ .....	1.47404	0.52300	161.085

$$\text{Dispersion (H}\gamma - \text{H}\alpha) = 4.770.$$

*Chaulmoogramide,  $C_{17}H_{31} \cdot CO \cdot NH_2$ .*

The amide was prepared according to Aschan's method (*Ber.*, 1898, 31, 2344), which consists in first converting the acid into its chloride by treating it with phosphorus trichloride, and then pouring the product into well-cooled, concentrated, aqueous ammonia. The white solid thus formed was thoroughly washed with water, dried, and crystallised several times from hot ethyl alcohol. It melted at  $106^\circ$ .

0.1039 gave 0.2942  $CO_2$  and 0.1112  $H_2O$ . C = 77.2 ; H = 11.9.

$C_{18}H_{33}ON$  requires C = 77.4 ; H = 11.8 per cent.

4.3 grams in 100 c.c. of chloroform gave  $\alpha_D + 1^\circ 14'$  in a 50 mm. tube, whence  $[\alpha]_D^{27^\circ} + 57.3^\circ$ .

*Ethyl Dibromodihydrochaulmoograte,  $C_{17}H_{31}Br_2 \cdot CO_2Et$ .*

Seventeen grams of ethyl chaulmoograte were dissolved in 50 c.c. of dry chloroform. To this solution, cooled below  $0^\circ$ , a solution of 9 grams of dry bromine in 30 c.c. of dry chloroform was gradually added in the absence of light ; the bromine was rapidly absorbed and without any evolution of hydrogen bromide. When all the bromine had been introduced, and after a lapse of several minutes, a permanent redness was apparent. After the removal of the slight excess of bromine by agitation with aqueous sodium hydrogen sulphite, the chloroform solution was washed, first with water, then with dilute aqueous sodium carbonate, again with water, and finally dried with calcium chloride. The chloroform was then removed by aspirating a rapid current of dry air through the liquid, which was maintained at  $25^\circ$ . The product was a nearly colourless oil, and was not markedly

unstable. A portion which had been exposed in a vacuum desiccator over paraffin wax was analysed:

0.3270 gave 0.2546 AgBr. Br = 33.1.

0.2634 „ 0.2050 AgBr. Br = 33.1.

$C_{20}H_{36}O_2Br_2$  requires Br = 34.1 per cent.

*Bromodihydrochaulmoogric Acid,  $C_{17}H_{32}Br \cdot CO_2H$ .*

Chaulmoogric acid (8.5 grams) was gently warmed in 25 c.c of a 68 per cent. solution of hydrogen bromide in glacial acetic acid, the mixture being maintained at 40—50° for about five minutes. On cooling, the liquid formed two layers, and the uppermost, which became solid, was accordingly separated, thoroughly washed with water, and finally dried on a porous plate; it was optically inactive, melted at 36—38°, and was shown by analysis to be bromodihydrochaulmoogric acid.

0.2102 gave 0.1040 AgBr. Br = 21.0

$C_{18}H_{33}O_2Br$  requires Br = 22.2 per cent.

*Action of Sodium and Amyl Alcohol on Chaulmoogric Acid. The Formation of Chaulmoogryl Alcohol,  $C_{18}H_{33} \cdot OH$ , and Chaulmoogryl Chaulmoograte,  $C_{17}H_{31} \cdot CO_2 \cdot C_{18}H_{33}$ .*

Thirty grams of chaulmoogric acid were dissolved in 750 c.c. of amyl alcohol and the solution boiled; six grams of sodium were then introduced, and the liquid vigorously heated until the metal had all dissolved. The solution was then acidified with sulphuric acid, well shaken, and the aqueous acid layer removed. The amyl-alcoholic solution was then washed several times with water, and again vigorously boiled and treated with a further 6 grams of sodium. This entire process was repeated six times. The amyl-alcoholic solution from the last treatment with sodium, after having been acidified with sulphuric acid and subsequently washed with water, was distilled in order to remove the greater part of the amyl alcohol. The remainder of the latter was eliminated by distillation in steam. The residue, which contained a supernatant layer, was extracted with ether, the ethereal solution being washed, dried, and the solvent removed. The product was then fractionally distilled under 18 mm. pressure, when the following fractions were obtained: (1) below 244° (a small amount); (2) 244—254° (15 grams); (3) 254—354° (1—2 grams); (4) 354—358° (5 grams). All these fractions became crystalline on cooling.



*Chaulmoogryl Alcohol*,  $C_{18}H_{33}\cdot OH$ .

*Fraction (1).*—This fraction, which was not entirely soluble in warm aqueous potassium hydroxide, was therefore saponified with the latter, and the undissolved crystalline substance dissolved in ether. The ethereal solution was then extracted several times with concentrated aqueous potassium hydroxide, washed with water, dried, and the solvent removed. The residual, colourless oil soon formed a hard, crystalline cake, which, after recrystallisation, first from acetone and then repeatedly from methyl alcohol, separated in long needles, melting sharply at  $36^{\circ}$ .

0.1016 gave 0.3016  $CO_2$  and 0.1162  $H_2O$ .  $C=81.0$ ;  $H=12.7$ .

0.1246 „ 0.3688  $CO_2$  „ 0.1430  $H_2O$ .  $C=80.7$ ;  $H=12.8$ .

$C_{18}H_{34}O$  requires  $C=81.2$ ;  $H=12.8$  per cent.

5.48 grams in 100 c.c. of chloroform gave  $\alpha_D + 1^{\circ}36'$  in a 50 mm. tube, whence  $[\alpha]_D + 58.4^{\circ}$ .

Chaulmoogryl alcohol is unsaturated, for it readily decolorises a solution of bromine in chloroform.

*Fraction (2).*—This was shown to consist entirely of chaulmoogric acid, no reduction to the dihydro-acid having taken place.

*Chaulmoogryl Chaulmoograte*,  $C_{17}H_{31}\cdot CO_2\cdot C_{18}H_{33}$ .

*Fractions (3) and (4).*—These were combined, dissolved in ether, the solution repeatedly extracted with aqueous potassium hydroxide, then with water, dried, and the solvent removed. The crystalline residue was recrystallised from ethyl acetate, from which it formed small, glistening rosettes, melting at  $42^{\circ}$ .

0.1430 gave 0.4272  $CO_2$  and 0.1572  $H_2O$ .  $C=81.5$ ;  $H=12.2$ .

$C_{36}H_{64}O_2$  requires  $C=81.8$ ;  $H=12.1$  per cent.

This substance was definitely shown to be chaulmoogryl chaulmoograte by the fact that on hydrolysis it afforded on the one hand chaulmoogric acid and on the other chaulmoogryl alcohol, both of which were identified by their properties and by analysis.

*Reduction of Bromodihydrochaulmoogric Acid with Zinc Dust and Alcohol. Formation of Dihydrochaulmoogric Acid*,  $C_{17}H_{33}\cdot CO_2H$ .

To a warm solution of 175 grams of bromodihydrochaulmoogric acid in alcohol, 60 grams of zinc dust were gradually added, and, after the introduction of the whole of the latter, the mixture was heated during

two hours in a reflux apparatus on a water-bath. The alcohol was then removed, the residue, which contained zinc salts, was treated with boiling aqueous potassium hydroxide to decompose the latter, subsequently acidified with sulphuric acid, and the liberated acids extracted with ether, the ethereal solution being washed, dried, and the ether removed. The product was then treated with a 68 per cent. solution of hydrogen bromide in glacial acetic acid, as described on p. 856 for the preparation of bromodihydrochaulmoogric acid. This is necessary in order to reconvert into a bromo-acid the unsaturated acid formed from bromodihydrochaulmoogric acid by the action of the zinc oxide contained in the zinc dust employed. The product from the treatment with hydrogen bromide was then dissolved in alcohol, again subjected to the action of zinc dust, as described above, and this entire operation was repeated six times.

The final product contained a saturated acid in preponderating amount, and, after distillation under diminished pressure, which removed some less volatile condensation product, was crystallised several times from glacial acetic acid saturated with hydrogen bromide. In this way, the last traces of unsaturated acids were eliminated, and the dihydro-acid was obtained in glistening leaflets which, after a final crystallisation from ethyl acetate, melted sharply at 71—72°, and this melting point was not altered by further crystallisation.

0.1370 gave 0.3840 CO<sub>2</sub> and 0.1520 H<sub>2</sub>O. C = 76.4 ; H = 12.3.

0.1000 „ 0.2804 CO<sub>2</sub> „ 0.1098 H<sub>2</sub>O. C = 76.5 ; H = 12.2.

0.1101 „ 0.3082 CO<sub>2</sub> „ 0.1218 H<sub>2</sub>O. C = 76.3 ; H = 12.3.

C<sub>18</sub>H<sub>34</sub>O<sub>2</sub> requires C = 76.6 ; H = 12.1 per cent.

Dihydrochaulmoogric acid boils at 248°/20 mm. and is optically inactive ; it is a saturated acid, since permanganate is entirely without action on it, and its solution in chloroform does not decolorise the slightest trace of bromine in the same solvent.

*Methyl Dihydrochaulmoograte*, C<sub>17</sub>H<sub>33</sub>·CO<sub>2</sub>Me.

This ester was readily obtained by dissolving dihydrochaulmoogric acid in methyl alcohol, adding concentrated sulphuric acid, and allowing the reaction to proceed for several hours. The ester, which formed a solid layer on the surface of the cold liquid, was extracted with ether, the ethereal solution being washed successively with aqueous sodium carbonate and water, dried, and the solvent removed. It was then distilled, when it passed over at 222—223°/20 mm. as a colourless oil, which, on cooling, formed a hard, crystalline mass melting at 26—27°.

0.1316 gave 0.3708 CO<sub>2</sub> and 0.1442 H<sub>2</sub>O. C = 76.8 ; H = 12.2.

0.0904 „ 0.2554 CO<sub>2</sub> „ 0.0994 H<sub>2</sub>O. C = 77.0 ; H = 12.2.

C<sub>19</sub>H<sub>36</sub>O<sub>2</sub> requires C = 77.0 ; H = 12.2 per cent.



*Action of Hydriodic Acid on Chaulmoogric Acid. Formation of Dihydrochaulmoogric Acid and a Hydrocarbon, Chaulmoogrene.*

Chaulmoogric acid, in quantities of 15 grams for each experiment, was mixed with 20 grams of hydriodic acid (sp. gr. 1.9) and 3 grams of amorphous phosphorus, and the mixture heated in a sealed tube at 200° during three hours. By working up the product in the usual manner, one obtained: (a) a mixture of acids, from which, after much difficulty, a very small amount of dihydrochaulmoogric acid was isolated, and (b) a neutral oil. The acid was analysed:

0.1693 gave 0.4710 CO<sub>2</sub> and 0.1836 H<sub>2</sub>O. C = 75.9; H = 12.0.

0.1013 „ 0.2820 CO<sub>2</sub> „ 0.1114 H<sub>2</sub>O. C = 75.9; H = 12.2.

0.1030 „ 0.2886 CO<sub>2</sub> „ 0.1110 H<sub>2</sub>O. C = 76.4; H = 12.0.

C<sub>18</sub>H<sub>34</sub>O<sub>2</sub> requires C = 76.6; H = 12.1 per cent.

The neutral oil was fractionally distilled under diminished pressure, and, finally, many times over sodium, until the latter remained unchanged; it then passed over at 193—194°/20 mm. as a colourless liquid, which was optically inactive.

0.1353 gave 0.4271 CO<sub>2</sub> and 0.1643 H<sub>2</sub>O. C = 86.1; H = 13.5.

0.0940 „ 0.2980 CO<sub>2</sub> and 0.1170 H<sub>2</sub>O. C = 86.4; H = 13.8.

C<sub>18</sub>H<sub>34</sub> requires C = 86.4; H = 13.6 per cent.

The analyses show that this substance is a hydrocarbon; it is accordingly designated chaulmoogrene.

When it was attempted to fuse chaulmoogric acid with either potassium or sodium hydroxide, no satisfactory result could be obtained, owing to the insolubility of the respective salts of the acid in the fused alkali hydroxides, from which they separated in solid lumps which were not attacked even at 300°.

*Oxidation of Chaulmoogric Acid with Potassium Permanganate (O = 1 atomic equivalent). Formation of Dihydroxydihydrochaulmoogric Acid, C<sub>17</sub>H<sub>31</sub>(OH)<sub>2</sub>·CO<sub>2</sub>H.*

One hundred grams of chaulmoogric acid were dissolved in a solution of 150 grams of potassium hydroxide in 7 litres of water. To this solution, the temperature of which throughout the operation was between 10° and 14°, a dilute solution of 40 grams of potassium permanganate was gradually added. Oxidation took place rapidly, and when all the permanganate had been introduced the mixture was allowed to remain for some time, and the precipitated oxide removed

by filtration. The filtrate was then concentrated and acidified with sulphuric acid, when a white, solid substance separated. This was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. The solid residue was then extracted with light petroleum, which removed a small amount of unchanged chaulmoogric acid. The portion insoluble in petroleum was crystallised repeatedly from warm benzene, then from acetone, ethyl acetate, and, finally, again from acetone, from which it separated in aggregates of fine needles, melting at  $102^{\circ}$ .

0.1068 gave 0.2680  $\text{CO}_2$  and 0.1042  $\text{H}_2\text{O}$ .  $\text{C} = 68.5$  ;  $\text{H} = 10.8$ .

0.1112 „ 0.2782  $\text{CO}_2$  „ 0.1068  $\text{H}_2\text{O}$ .  $\text{C} = 68.2$  ;  $\text{H} = 10.7$ .

$\text{C}_{18}\text{H}_{34}\text{O}_4$  requires  $\text{C} = 68.8$  ;  $\text{H} = 10.8$  per cent.

*Oxidation of Chaulmoogric Acid with Potassium Permanganate (O = 4—5 atomic equivalents). Formation of Formic Acid and Two Dibasic Acids,  $\text{C}_{17}\text{H}_{30}\text{O}_4$  and  $\text{C}_{17}\text{H}_{30}\text{O}_5$ .*

When chaulmoogric acid, dissolved in dilute aqueous potassium hydroxide, was oxidised at the ordinary temperature with an amount of permanganate equivalent to 4—5 atomic proportions of oxygen, the following substances were produced :

(a) Formic acid, which was isolated in the form of its barium salt and the latter analysed.

(b) A mixture of several other acids, which were converted into their ethyl esters. On distilling these under diminished pressure (10 mm.), they yielded the following fractions :

(1)  $210\text{—}220^{\circ}$  ; (2)  $220\text{—}260^{\circ}$  ; (3)  $260\text{—}270^{\circ}$  ; and (4)  $270\text{—}280^{\circ}$ , a very small amount.

*Fraction (1).*—This, which became crystalline on cooling, was drained from a little adhering oil and then crystallised from methyl alcohol, from which it separated in shining leaflets, melting at  $26\text{—}27^{\circ}$ .

0.0724 gave 0.1882  $\text{CO}_2$  and 0.0710  $\text{H}_2\text{O}$ .  $\text{C} = 70.9$  ;  $\text{H} = 10.9$ .

0.0622 „ 0.1608  $\text{CO}_2$  „ 0.0606  $\text{H}_2\text{O}$ .  $\text{C} = 70.5$  ;  $\text{H} = 10.8$ .

$\text{C}_{21}\text{H}_{38}\text{O}_4$  requires  $\text{C} = 71.2$  ;  $\text{H} = 10.7$  per cent.

0.5140 required  $\text{NaOH}$  equivalent to 29.1 c.c. of a decinormal solution, instead of 29 c.c., the calculated amount for  $\text{C}_{15}\text{H}_{28}(\text{CO}_2\text{Et})_2$

A silver salt of the corresponding acid was prepared from the sodium salt.

0.1728 gave 0.0718  $\text{Ag}$ .  $\text{Ag} = 41.6$ .

$\text{C}_{17}\text{H}_{28}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 42.3$  per cent.

It was thus shown that the fraction of ester boiling at



210—220°/10 mm. consisted of the diethyl ester of a dibasic acid having the formula  $C_{17}H_{30}O_4$ .

*Fraction (3).*—This slowly deposited a small quantity of a crystalline ester which, when crystallised from light petroleum, separated in needles, melting at 53°.

0.0974 gave 0.2420  $CO_2$  and 0.0884  $H_2O$ .  $C = 67.7$ ;  $H = 10.1$ .

0.0972 „ 0.2416  $CO_2$  „ 0.0892  $H_2O$ .  $C = 67.8$ ;  $H = 10.2$ .

$C_{21}H_{38}O_5$  requires  $C = 68.1$ ;  $H = 10.3$  per cent.

0.3722 required NaOH equivalent to 20.7 c.c. of a decinormal solution, instead of 20.1 c.c., the calculated amount for  $C_{15}H_{28}O(CO_2Et)_2$ .

By the hydrolysis of this ester (m. p. 53°), the corresponding acid was obtained, which, on recrystallisation from ether, formed glistening laminae, melting at 128°.

0.1200 gave 0.2852  $CO_2$  and 0.1012  $H_2O$ .  $C = 64.8$ ;  $H = 9.4$ .

0.0740 „ 0.1756  $CO_2$  „ 0.0620  $H_2O$ .  $C = 64.6$ ;  $H = 9.3$ .

$C_{17}H_{30}O_5$  requires  $C = 65.0$ ;  $H = 9.5$  per cent.

0.4576 required NaOH equivalent to 29.5 c.c. of a decinormal solution, instead of 29.2 c.c., the calculated amount for a dibasic acid having the formula  $C_{17}H_{30}O_5$ .

The silver salt was prepared from the sodium salt.

0.1982 gave 0.0806 Ag.  $Ag = 40.6$ .

0.0996 „ 0.1412  $CO_2$ , 0.0472  $H_2O$ , and 0.0400 Ag.

$C = 38.6$ ;  $H = 5.3$ ;  $Ag = 40.2$ .

$C_{17}H_{28}O_5Ag_2$  requires  $C = 38.6$ ;  $H = 5.3$ ;  $Ag = 40.8$  per cent.

It was thus proved that this acid is a dibasic acid having the formula  $C_{17}H_{30}O_5$ .

The products of the oxidation of chaulmoogric acid are being further investigated, and will be more fully described and characterised in the next communication on this subject.

We desire to express our thanks to Mr. F. H. Lees for the valuable aid he has given us throughout this investigation.

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